

### **IV.E.3. Advanced MEAs for Enhanced Operating Conditions**

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#### **Objectives**

Develop high performance, lower cost membrane electrode assemblies (MEAs) that

- meet demanding system operating conditions of higher temperature with little or no humidification,
- use less precious metal than current state-of-the-art constructions, and
- are made by processes amenable to high volume manufacturing.

#### **Technical Barriers**

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- Q. Electrode Performance
- R. Thermal and Water Management

#### **Approach**

- Develop advanced cathode catalysts that have less precious metal and can be made by high volume compatible processes, building on the knowledge gained in the preceding 3M/DOE Cooperative Agreement, DE-FC02-99EE50582.
- Develop membranes that are stable at operating conditions of  $85 < T < 120^{\circ}\text{C}$ , based on 3M's hydrophilic ionomers that have shown greater stability at these temperatures than current commercial membranes. Optimize matching MEA components, flow field, and air management for these operating conditions.
- Develop high temperature non-aqueous electrolyte membranes, stable catalyst constructions, optimized catalyst/membrane interfaces, and matching gas diffusion layer and flow field components for an operating range of  $120 < T < 150^{\circ}\text{C}$  and nearly dry operation.
- Scale up and optimize MEA component fabrication processes amenable to high volume, high quality, low cost production for selected components from the above tasks.
- Characterize selected MEAs in full-scale, short stacks.

## Accomplishments

- Demonstrated reduced F<sup>-</sup> ion generation and longer lifetime of 3M's perfluorinated sulfonic acid ionomeric membrane compared with standard proton exchange membrane (PEM) ionomer.
- Developed a "liquid H-pump" technique to measure the proton conductivity of ionic liquids and acids.
- Developed liquid mixtures with no added water having proton conductivities of 40 mS/cm at 120°C with no water, which is 100 to 1000 times greater than anhydrous acids.
- Demonstrated a membrane additive that reduces membrane weight loss occurring during a peroxide soak test by over a factor of 100 compared to a standard ionomer control.
- Developed cathode catalyst compositions and structures having higher performance at a Pt loading of 0.1 mg/cm<sup>2</sup> than the baseline, using 3M nanostructured catalyst processes amenable to high volume manufacture.
- Demonstrated higher chemical oxidative stability of the 3M nanostructured film supported catalysts compared with commercial carbon black supported Pt catalysts.
- Demonstrated higher electrochemical stability of surface area and double layer capacitance of nanostructured ternary catalysts under either highly oxidative thermal or electrochemical potential conditions compared to carbon black supported catalysts.

## Future Directions

- Continue the membrane and cathode catalyst development and screening and the fabrication and testing of integrated catalyst coated membranes (CCMs).
- Optimize gas diffusion layers, flow fields, and air management to match the CCMs for higher temperature operation, building on previously developed computational models and test results.

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## Introduction

Proton exchange membrane fuel cells (PEMFCs) have been developed sufficiently to demonstrate their feasible use for automotive and distributed stationary applications. However, several issues must be addressed to demonstrate commercial viability, including efficiency, durability, and cost. Overall, system efficiency is the critical factor affecting fuel usage and operating costs. The efficiency of a fuel cell is directly related to the cell operating voltage. The higher the voltage, the higher the efficiency, but the current density and power available are then lower, which affects stack size and cost. These factors are primarily affected by polarization of the cathode catalyst and stability of catalyst activity and surface area. Therefore, higher performing and more stable cathode catalysts are required to achieve the goals of increased performance with less precious metal catalyst. From a system perspective, operation at higher temperatures reduces thermal management

constraints, thereby increasing overall efficiency. Greater tolerance of fuel impurities at high temperatures can also contribute to performance increases and, potentially, to lower costs of fuel processing components. However, the humidification requirements for higher temperature operation are significant. Designing an MEA to operate under hot, dry, pressurized conditions requires development of new membranes, catalysts and gas diffusion layers that are stable and durable at those conditions. The components must be matched to each other and integrated with a flow field design and air management strategy. In addition, the processes for making the MEA components must be consistent with high volume production. This project is directed toward development of MEAs that meet demanding system operating conditions of higher temperature and little or no humidification, use less precious metal than current state-of-the-art constructions, and are made by processes amenable to high volume manufacturing.

## **Approach**

The approach to higher temperature MEAs on this project involves the development of components for two sets of temperature ranges:  $85 < T < 120^{\circ}\text{C}$  and  $120 < T < 150^{\circ}\text{C}$ . For the lower temperature range, proton exchange membranes are being developed based on modifications of existing perfluorinated sulfonic acid (PFSA) type membranes that still rely on water for proton conduction, such as Nafion™ or 3M's PFSA ionomeric membrane. These modifications include incorporation of functionalized additives to facilitate peroxide decomposition for better oxidative stability and enhanced water retention for higher conductivity under low humidification. For the higher temperature range, new membrane materials and non-water based proton conduction methods are being investigated, which utilize 3M perfluorinated acids, various proprietary liquids, and various inorganic additives. Work includes understanding how to incorporate those materials into polymer matrices to form effective membranes. The polymer matrices and process methods include both new and existing materials and methods.

The approach to the development of advanced cathode catalysts that have less precious metal than current state-of-the-art constructions builds on the knowledge gained in 3M/DOE Cooperative Agreement DE-FC02-99EE50582. Cathode catalysts that significantly outperformed pure Pt were made using a 3M nanostructured, thin film catalyst support system and catalyst deposition process, which easily generates new compositions and structures via a dry, roll-goods process (roll-goods are made by a semi-continuous process and stored on a roll) amenable to high volume manufacturing. (See FY 2003 Progress Report on the above contract and also References 1 and 2.) The catalyst structures and PtAB ternary materials developed under that contract exhibit unique electronic features and increased surface area. The 3M nanostructured thin film supports (carbon free) show less susceptibility to oxidation and loss of catalyst surface area under highly oxidative conditions than commercially available carbon supported dispersed catalysts. Methods for generating new catalyst constructions include pilot-line production of large area catalyst formulations and a combinatorial method for generating and characterizing a wide

latitude of ternary and quaternary compositions and structures using similar thin film catalyst deposition methods (with subcontractor Dalhousie University). Conventional dispersed catalysts with improved oxidatively stable carbon supports are also being investigated.

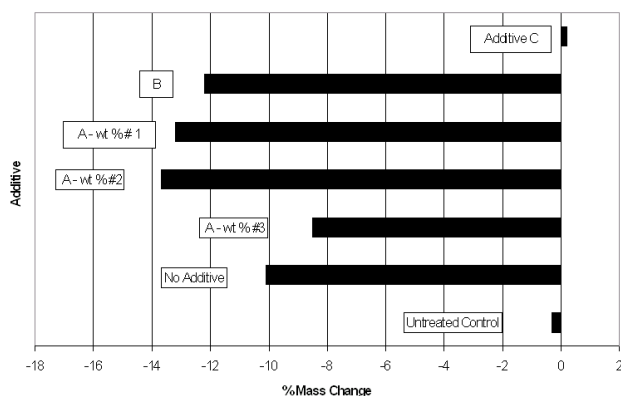
For all the enhanced membrane and catalyst materials and process development work, a suite of critical property measurements is employed to guide development and down-selection of approaches. These include methods to measure the ionic and proton conductivity of the membranes, electrochemical impedance spectroscopy, chemical stability, PEM physical and mechanical properties, catalyst electrochemical surface areas and activities, and fuel cell tests under various protocols. Finally, methods to form effective interfaces of the catalysts with the new membranes for both operating temperature ranges are necessary for optimum MEA performance.

## **Results**

As part of the effort to develop a more stable PEM for the range of  $85^{\circ}\text{C} < T < 120^{\circ}\text{C}$ , a series of nearly 60 composite membranes was fabricated based on addition of inorganic dispersions to Nafion™ in order to enhance water uptake. Extensive resistance testing by hydrogen pump and high frequency impedance at  $120^{\circ}\text{C}$ , ambient pressure and  $80^{\circ}\text{C}$  dew point showed the effect of the majority of these additives was to make the resistance worse than the Nafion™ control. Two of the additives made slight improvements under these challenging conditions. More recently, some of these same additives have been incorporated into the 3M ionomeric membrane. As shown in Reference 3, under identical test conditions of  $80^{\circ}\text{C}$  cell,  $0.35\text{ A/cm}^2$ , and  $\text{H}_2/\text{air}$  at 27%/27% relative humidity (RH), 3M roll-good fabricated membranes using 3M's own PFSA ionomer had an 80% increase in lifetime over 3M fabricated membranes made with Nafion™ 1000 ionomer. It is expected that incorporation of the right functionalized additives to the 3M ionomer should further enhance these stability properties and maintain conductivity with less humidification. This work will now focus on this new ionomer.

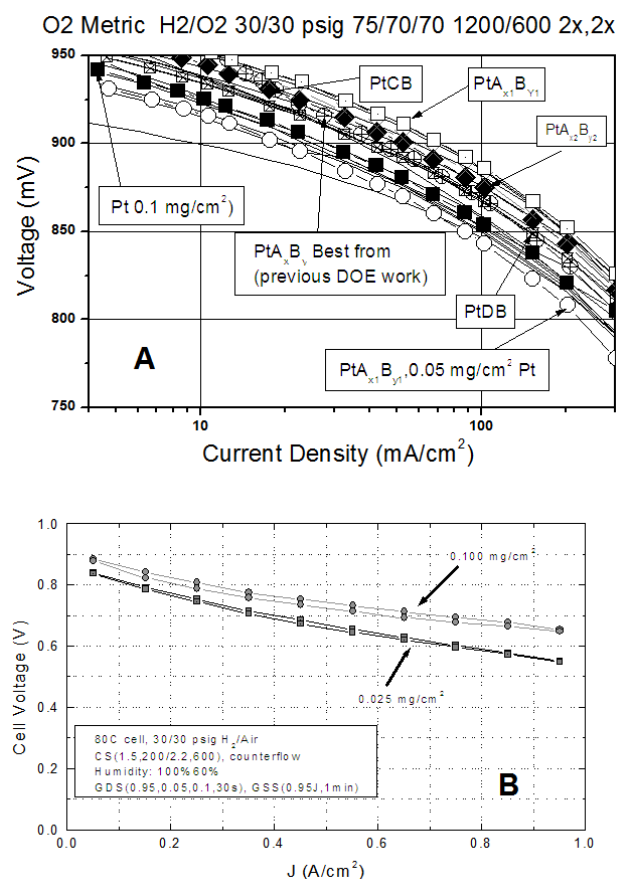
Peroxide generated at the anode in PEMFCs due to oxygen crossover is a serious mode of membrane degradation at high temperatures and dry conditions (Reference 4). Significant progress has been made developing and applying methods to evaluate the activity of membrane additives for peroxide decomposition. The key method uses weight loss measurements of membranes soaked in peroxide solutions for prolonged periods of time. Using literature and proprietary approaches, additives have been identified and screened for addition to the PFSA ionomers which, in addition to reducing weight loss in these accelerated tests, must not negatively impact ionic conductivity, electronic resistance, or fuel cell performance of the resulting MEAs. Figure 1 illustrates the membrane mass loss of various additives versus controls, showing that Additive C can reduce the mass loss from the -10% seen for the non-additive control to zero within the  $\pm 0.1\%$  error of the measurement. Fuel cell performance and  $F^-$  ion release rates are being evaluated.

A total of 53 different Pt based ternary cathode catalysts have been fabricated on large area, roll-good capable pilot-line equipment and evaluated by various fuel cell tests. The catalysts, all made on the 3M nanostructured support films, differ by composition, non-noble metal type, and a structure factor tied to the catalyst deposition process. All have  $0.1 \text{ mg/cm}^2$  of Pt or less and for screening



**Figure 1.** Comparison of the effect of various additives on PFSA membrane mass loss upon exposure to  $1 \text{ M H}_2\text{O}_2$  at  $90^\circ\text{C}$  for 120 hours (refreshed every 24 hours), showing that one, Additive C, can reduce the mass loss from -10% seen for the non-additive control to zero within the  $\pm 0.1\%$  error of the measurement.

purposes are tested with standard PFSA membranes. Figure 2 (top) illustrates comparative polarization curves under a pressurized oxygen test protocol for comparing the activity of the various catalysts, showing many performing better than pure Pt. Figure 2 (bottom) illustrates the range of precious metal loadings under investigation and the effect on  $\text{H}_2/\text{air}$  fuel cell performance for one  $\text{PtA}_x\text{B}_y$  construction. The anode catalyst is  $0.14 \text{ mg Pt/cm}^2$  in each case of Figure 2 (bottom). A four-fold



**Figure 2.** (A) Comparison of high pressure oxygen metric polarization curves from various nanostructured thin film ternary catalysts with  $0.1 \text{ mg/cm}^2$  of Pt, unless noted. (B) Comparison of pressurized, constant stoichiometry (CS), constant current, polarization curves for two  $\text{PtAB}$  cathode catalyst constructions having  $0.100$  and  $0.025 \text{ mg Pt/cm}^2$ , with  $0.14 \text{ mg/cm}^2$  of pure Pt on the anode. Cell  $T = 80^\circ\text{C}$ , 30/30 psig, 1.5/2.2  $\text{H}_2/\text{air}$  stoichiometry, galvanodynamic scans (GDS), 100%/60% anode/cathode inlet RH,  $50\text{-cm}^2$  quad-serpentine flow field.

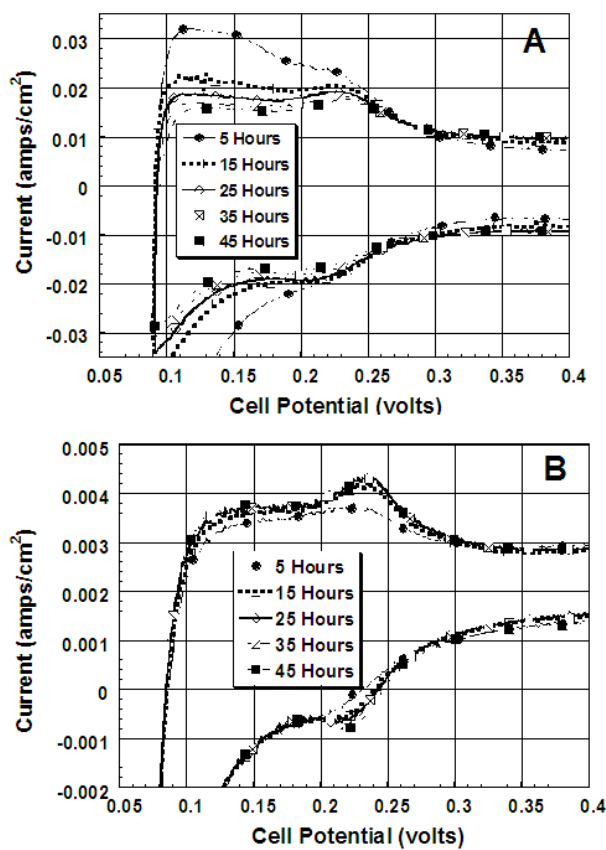
reduction in cathode loading has cost approximately 50 – 100 mV of cell performance over the 0.1 to 0.9 A/cm<sup>2</sup> current range and illustrates the challenge of the DOE targets of 0.05 mg/cm<sup>2</sup> total per MEA producing 0.5 A/cm<sup>2</sup> at 0.8 V.

Significant progress has been made with our Dalhousie University subcontractor in applying combinatorial methodology for fabricating 50-cm<sup>2</sup> sized arrays of continuously varying catalyst compositions and structures, applied to the 3M nanostructured support films. A dozen of these catalyst arrays have been fabricated in triplicate and characterized by scanning X-ray diffraction and electron microprobe, formed into MEAs at 3M and tested using combinatorial and segmented cell screening methods as well as larger fuel cell tests. Baseline data have been obtained to establish the degree of correlation between the subcontractor's and 3M's deposition processes and identify issues with the combinatorial and segmented cell screening analyses that need to be resolved in order to usefully reveal catalyst activity differences seen in single cell constructions.

Under high temperature and dry conditions, stability of all the MEA components is a challenge. The catalyst activity, its surface area and its support particle must all be stable, both chemically and electrochemically, particularly against oxidation. The thermal stability of the 3M nanostructured film supported catalysts was shown to be significantly greater than commercially available carbon supported Pt catalysts, using highly sensitive thermal gravimetric analysis weight-loss profiles over 20 hours at 170°C in air (see Reference 3). *In-situ* fuel cell measurements of catalyst electrochemical surface area (ECSA) before and after 90 hours under 120°C, 30 psig H<sub>2</sub>/air, and constant current conditions have shown a negligible loss in surface area for the 3M ternary catalysts, compared to a 42% loss in 70 hours from carbon supported Pt catalysts. More recent characterization of oxidative stability was completed by voltammetric polarization of cells to 1.2 V for 5 hours at 80°C under saturated H<sub>2</sub>/N<sub>2</sub>, followed by complete cyclic voltammetry scans for ECSA measurements. As shown in Figure 3, over approximately 50 hours, the conventional dispersed carbon supported catalysts' ECSA decreased significantly and progressively after each 5 hour

period while its double layer capacitance increased, indicating carbon oxidation. In contrast, the 3M nanostructured film supported Pt catalysts' ECSA progressively increased, consistent with catalyst clean-up, and the double layer capacitance was essentially unchanged, consistent with the increased thermal stability of the 3M catalyst support system. The loss of surface area is shown to be directly related to fuel cell performance, and the rate of surface area loss is temperature dependent.

Good progress towards development of a high temperature membrane (120 < T < 150°C) that does not rely on water for proton conduction has been

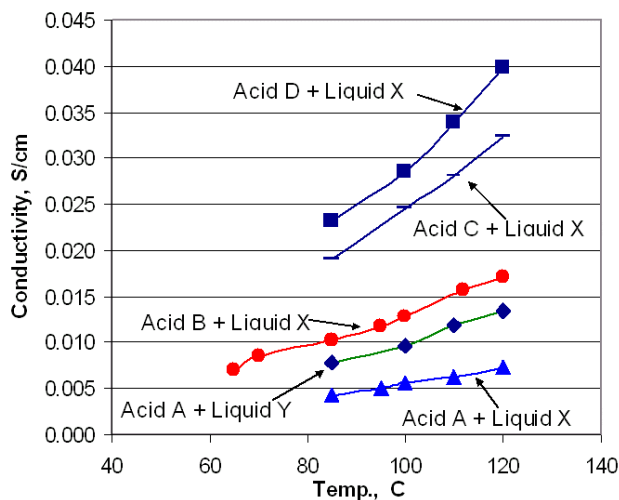


**Figure 3.** Comparison of cyclic voltammograms from (A) carbon supported Pt and (B) 3M nanostructured film supported Pt, taken every five hours during which the cell was polarized to 1.2 V at 80°C under saturated H<sub>2</sub>/N<sub>2</sub>. The ECSA of the C/Pt catalyst decreased with time, and its double layer capacitance increased. The opposite is true for the 3M nanostructured film supported catalyst.

realized through both development of critical characterization techniques and new materials synthesis. High proton conductivity, as opposed to a more general ionic conductivity measured by AC impedance techniques, in the absence of water is a first requirement for such materials, and a methodology was developed to measure the proton conductivity of liquid based cells containing the new electrolyte candidates. Figure 4 compares the proton conductivity as a function of temperature in the absence of water of five different combinations of fluorinated acids and liquid additives, none of which involves phosphoric acid. As seen, the combination of acid D with liquid X has already at 120°C produced conductivity sufficient for acceptable fuel cell performance at lower temperatures with standard PEMs. Work has recently begun on incorporating these proton conductive materials into useable solid polymer membranes and addressing the issues of forming effective catalyst/ionomer interfaces. More conventional high frequency impedance measurements of these membranes agree with the liquid cell proton conductivity measurements.

### Conclusions

The 3M PFSA ionomeric membrane has shown longer lifetime and improved mechanical properties



**Figure 4.** Illustration of the proton conductivity, measured in a special liquid cell with proton injection, of five different electrolyte combinations of perfluorinated acids and liquid additives, with no water in the system. The target range for adequate proton conductivity is  $\geq 0.030$  S/cm.

over membranes made with current commercial PEM ionomers for operation in the temperature range  $85 < T < 120^\circ\text{C}$ . There is the opportunity for further improvement with key additives. For the range  $120 < T < 150^\circ\text{C}$ , the approach to development of new membranes using perfluorinated acids plus liquid additives is promising, based on actual proton conductivity results. Key issues will revolve around forming useful membranes and effective catalyst/electrolyte interfaces with these new materials. The oxidative chemical stability and high temperature electrochemical surface area stability of 3M nanostructured catalysts and supports appear to be better than those of commercial carbon black supported Pt catalysts. The 3M nanostructured catalyst process and combinatorial approach to development of new catalysts are continuing to yield catalyst constructions having improved performance with lower loadings.

### References

1. Hydrogen, Fuel Cells, and Infrastructure Technologies FY 2002 Progress Report, page 379.
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3. 2003 DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review Meeting, May 19 - 22, 2003, Berkeley, CA, Project 72.
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### FY 2003 Publications/Presentations

1. 2003 DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review Meeting, May 19 - 22, 2003, Berkeley, CA, Project 72.